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# (54) Cathodic electro-deposition coating composition and process

(57) An aqueous coating composition for use in coating substrates such as automobile bodies and body components by cathodic electro-deposition contains, in addition to a cationic binder resin and a dispersed fusible solid thermosetting resin powder, a curing agent for heat curing the cationic binder resin. The weight of thermo-setting resin powder is 10—100%, preferably 50—100%, of the weight of cationic binder resin plus curing agent therefor. The coating is applied in an electro-coating bath, generally at a voltage of 100 to 500 volts and is cured by heating at a temperature usually in the range 150 to 250°C.

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SPECIFICATION

**Cathodic electro-deposition coating composition and process**

This invention relates to a process for coating a substrate with a synthetic resin coating composition by cathodic electro-deposition and to a coating composition suitable for use in such a process.

Electro-deposition is a coating process of increasing commercial importance. The earliest coating compositions for electro-deposition were anionic and generally contained a synthetic resin having carboxylic acid groups and carrying a negative charge which was deposited at the anode. More recently cationic compositions which deposit a synthetic resin at the cathode have been developed and there are now preferred for many uses because of their higher throwing power, that is their ability to coat areas of the substrate electrode which are remote or shielded from the other electrode. Cathodic electro-deposition is also preferred because metal ions are generally evolved at the anode in electro-coating and may cause defects in the freshly deposited coating.

The major use of electro-deposited coatings is as a first coat for car bodies and parts thereof. Electro-coating generally deposits a paint layer of dry film thickness of 15—20 microns. The electro-coated car body is generally subsequently coated with a further undercoat applied by conventional means, for example by spraying a solvent based paint. This coat, known as the surfacer coat, is required to build up film thickness before the top colour coat is applied.

Electro-coating has had an important effect in reducing corrosion to car bodies by coating hidden parts which other types of coating cannot reliably reach; so much so that the most troublesome form of corrosion in many cars is that known as 'scab' corrosion in which a small area of the surface of the car body becomes rusted where there has been mechanical damage, for example chipping, of the paint. The thin paint films deposited by electro-coating are not very effective in helping to resist this type of corrosion and an electro-coating process which deposits a thicker and tougher film would be desirable.

British Patent 1,407,410 describes and claims a process for coating an electrically conductive article with a resinous material by electro-deposition which comprises immersing the article as the cathode in an aqueous electro-deposition bath containing a cationic binder resin and a non-ionic synthetic resin powder dispersed therein, the amount of the non-ionic resin being 100 to 5000 parts by weight per 100 parts of the binder resin, applying a voltage between the cathodic article and an anode to cause electric current to flow through the bath so that a resinous coating comprising the binder resin and non-ionic resin powder is electrodeposited on the cathodic article, removing the coated article from the bath and baking the article to form an adherent resinous film thereon. This coating process produces a coating which is essentially a powder coating and is tougher than the previously known electrodeposited coatings in which the cationic binder resin is the only film forming resin. However, the process of British Patent 1,407,410 loses many of the advantages of electro-coating. The way in which the paint film is deposited appears to be different from normal electro-coating. The process of British Patent 1,407,410 very rapidly deposits a thick coating, for example up to 100 microns in 15 seconds and increasing with further time, whereas a normal electro-coating process is self-regulating in the coating thickness formed. Abnormally high thicknesses of paint are deposited on any area of a phosphated steel substrate, for example a car body, which has been accidentally touched before electro-deposition. The coating deposited is much richer in the resin powder compared to the cationic binder resin than is the electro-coating bath. The coating compositions described in British Patent 1,407,410 have a very low throwing power giving little or no cover to surfaces remote or hidden from the anode. It may even be necessary to use auxiliary electrodes to give adequate coating around sharp edges. The electro-deposition process has to be followed by a second electro-coating process to coat the surfaces not reached, such as a box section of a car body, as described in German Patent Specification 2,919,129. In effect the process of British Patent 1,407,410 is a method of applying a powder coating by electro-deposition rather than an electro-coating process having the usual advantages of electro-coating.

The present invention seeks to provide an electro-coating process and composition which substantially retains the advantages of electro-coating but deposits a tougher film.

An aqueous coating composition according to the invention suitable for cathodic electro-deposition comprises a cationic binder resin, a curing agent for heat curing the cationic binder resin after electro-deposition and a fusible solid thermo-setting resin powder dispersed in the coating composition, the weight of thermo-setting resin powder being 10 to 100 *per cent* based on the weight of the cationic binder resin and the curing agent therefor.

A process according to the invention for coating an electrically conductive substrate comprises immersing the substrate as cathode in an electro-coating bath of an aqueous coating composition according to the invention, applying a voltage of 100 to 500 volts between an anode in the bath and the cathode substrate to deposit a coating of the cationic binder resin, the curing agent and the thermo-setting resin powder on the substrate, removing the coated substrate from the bath and heating it at a temperature in the range 150 to 250°C to cure the cationic binder resin and to fuse and cure the thermo-setting resin powder.

The process of the invention generally gives rise to a coating of dry film thickness 20 to

60 microns. The maximum thickness deposited is self-regulating as with known electro-paints containing no resin powder and varies little over a wide range of voltages. For coating steel automobile bodies and body components the coating composition preferably contains 50—100% by weight thermo-setting resin powder based on the weight of the cationic binder resin and the curing agent therefor, forming a tough coating of thickness 30 to 60 microns, generally at least 40 microns. The automobile body or body component coated according to the invention can be over-coated with a colour top-coat without the need for an intermediate 'surfacer' coat.

The cationic binder resins generally contain amine groups to confer water dispersability and to allow the resin to carry a positive charge. The binder resin generally contains further reactive groups to promote curing, for example hydroxyl, epoxy and/or blocked isocyanate groups. Some of the amine groups in the binder resin can be in the form of quaternary ammonium groups. The binder resin can, for example, have a polyamide, polyester, epoxy, polyurethane, phenolic or acrylic polymer backbone or may have segments of two or more of these polymer types, for example an epoxy resin can contain polyester or polyether blocks. An epoxy resin or acrylic polymer backbone is preferred.

The curing agent for the cationic binder resin preferably contains blocked isocyanate groups which are unreactive with amine groups and other groups containing active hydrogen at ambient temperature but which become unblocked and reactive at the curing temperature. The curing agent can, for example, be a polyisocyanate, preferably an aliphatic polyisocyanate, whose isocyanate groups are blocked by reaction with a lactam. The binder resins preferably contain other functional substituents as well as amine groups which react with the curing agent, for example they preferably contain hydroxyl groups for better curing with a blocked isocyanate curing agent. An alternative curing agent reactive with hydroxyl groups is a fully or partially etherified melamine formaldehyde resin. An example of a curing agent reactive with amine groups is a phenolic terminated epoxy resin.

The incorporation of a curing agent for the binder resin in the electro-coating composition enables the binder resin to cure sufficiently to contribute substantially to the toughness of the coated film, so that the proportion of binder can be high enough to give good throwing power without losing the advantage of increased film toughness given by the powder resin.

One example of a preferred type of binder resin is an epoxy resin, for example a condensed glycidyl ether of a bisphenol, reacted with a hydroxyalkyl amine such as mono-ethanolamine or diethanolamine to introduce amine and hydroxyl groups. An alternative epoxy resin is the reaction product of an epoxy resin and a polyamine having both secondary and primary amine groups such as diethylene triamine and optionally also a hydroxyalkylamine such as mono- or di-ethanolamine. The epoxy amino resin product is substituted by $—N(RNH_2)_2$ groups, R being alkylene, in which the primary amine groups can participate in cross-linking reactions with for example a phenolic terminated epoxy resin. An alternative type of binder resin is an acrylic copolymer containing amine groups, for example a copolymer derived from an alkylaminoalkyl acrylate or methacrylate such as dimethylaminoethyl methacrylate, and preferably also containing hydroxyl groups, for example a copolymer derived additionally from a hydroxyalkyl acrylate or methacrylate such as hydroxyethyl methacrylate.

The fusible solid thermo-setting resin powder is preferably of the type used in powder coatings. It can be based on a self-crosslinking resin, but more usually the resin powder particles contain both a thermo-setting resin and a curing agent for it. The thermo-setting resin powder should be such that it fuses and cures at the temperature required for heat curing the cationic binder resin, 150 to 250°C according to the process of the invention.

Examples of preferred thermo-setting resins to be used as a basis for the fusible solid thermosetting resin powder are epoxy resins, polyesters and polyurethanes. Epoxy resins can be used in combination with various curing agents, for examine amine curing agents such as dicyandiamide, substitited dicyandiamides, imidazole and amino-containing polyamides, acid anhydrides, Lewis acids and Lewis bases. Polyester resins used in the fusible solid thermosetting resin powders can have free carboyxlic acid groups, in which case they can be cured by reaction with epoxy resins, or free hydroxyl groups, in which case they can be cured by reaction with amino formaldehyde resins or polyurethanes containing isocyanate groups, usually blocked isocyanate groups. Alternatively a polyurethane prepolymer containing blocked isocyanate groups can be the major resin of the thermo-setting resin powder, used with a polyol curing agent. Epoxy resin powders are preferred for use with cationic epoxy resin binders and polyurethane resin powders are preferred for use with cationic acrylic resin binders.

The fusible solid thermo-setting resin and the curing agent therefor can be composited by methods known in the production of powder coatings. For example, a thermo-setting resin and curing agent can be thoroughly mixed, melt composited at a temperature well below the curing temperature in a screw extruder or a Z-blade mixer, granulated and then ground to an appropriate particle size, preferably in the range 1 to 100 microns.

The amount of thermo-setting resin powder used is desirably 50 to 100 *per cent*, preferably 60 to 90 *per cent*, by weight based on the cationic binder resin and the curing agent therefor. If the thermo-setting resin powder content is increased above 100 *per cent* based on the cationic resin plus curing agent therefor the throwing power of the coating composition rapidly decreases.

The incorporation of the fusible thermo-setting resin powder in the coating composition improves the colour stability of the cured coating, particularly for light coloured coatings where yellowing or

browning of the cured coating would spoil the appearance.

The coating composition is preferably pigmented. In particular, the pigment is preferably included in the thermo-setting resin powder particles. Incorporation of a white or other light coloured pigment in the thermo-setting resin powder has a much greater effect in improving the colour of the cured electro-deposited coating than incorporation of the same amount of additional light coloured pigment dispersed in the resin. The thermo-setting resin powder can for example contain 5 to 50 *per cent*, most preferably 20—35 *per cent*, by weight of a light coloured pigment such as titanium dioxide, which is readily available in very small particle sizes requiring no further comminution before use in the thermo-setting resin powder. Pigment can also be dispersed in the aqueous cationic resin as well as or instead of in the thermo-setting resin powder. Examples of pigments which can be used are titanium dioxide, red and yellow chromium-containing pigments and organic pigments such as phthalocyanine pigments.

The thermo-setting resin component of the dispersed fusible solid thermo-setting resin powder is preferably selected so that it cross-links predominantly by reaction with the curing agent present in the resin powder particles rather than by reaction with the cationic binder resin or the curing agent used for the cationic binder resin, particularly when a light coloured coating is required.

The coating composition can contain more than one cationic binder resin, for example it can include a resin having amine groups which are in the form of quaternary ammonium groups as well as a resin having free (unquaternised) amine groups or it can include a cationic resin having a polymer structure very similar to that of the thermo-setting resin powder used as well as another cationic resin, the former cationic resin acting as a dispersion aid for the thermo-setting resin powder. However, this is not generally necessary. We have found that a cationic binder resin formed by reacting an epoxy resin with a hydroxyalkyl amine forms a well dispersed coating composition with a thermo-setting epoxy resin powder and also has good cationic and heat curing properties. The coating compositions of the invention, unlike compositions containing a much higher proportion of thermo-setting resin powder, can easily be re-dispersed by stirring even after three days' settling. To obtain maximum resistance to settling of the thermo-setting resin powder the coating composition is preferably ball milled after dispersion of the thermo-setting resin powder in the aqueous cationic binder resin. The final particle size of the thermo-setting resin powder is preferably in the range 1 to 50 microns.

The coating process according to the invention can be carried out using known apparatus for electro-coating with known means for recirculation and replenishing of the coating composition. The pH of the coating composition is preferably in the range 5 to 6.5, most preferably 6. This is the pH generally used for cationic electro-deposition and allows the use of mild steel pipe work and vessels in the recirculation apparatus, whereas the coating compositions of British Patent 1,407,410 need to be used at a pH of 4 to 4.5. The article to be coated is arranged to be a cathode and is dipped in the electro-coating bath, the time of immersion being preferably 20 to 180 seconds. The electro-coated article is rinsed and then stoved at a temperature suitable for curing the cationic binder resin. A temperature in the range 170 to 185°C is preferably used for curing an amine-containing cationic resin by reaction with a blocked polyisocyanate.

The coating deposited on the article being coated in the electro-coating bath is somewhat richer in thermo-setting resin powder, and in pigment if used, compared to the cationic binder resin than is the electro-coating bath. The coating composition used to replenish the electro-coating bath should be formulated to take account of this. The difference in the ratio of resin powder to cationic binder resin between the coating deposited and the electro-coating bath is much less than in the process described in British Patent 1,407,410. Surprisingly, if the coating composition of the present invention is applied at a very low voltage, such as 50 volts, it deposits a coating which is much richer in resin powder and whose thickness is less controllable than when applied at 100 to 500 volts according to the process of the invention. The voltages generally preferred for electro-deposition, particularly on automobile bodies, are in the range 250 to 400 volts.

The throwing power of coating compositions according to the invention is generally as good as that of the best commercial anodic electro-coating compositions. In most cases this is sufficient to cover remote and shielded parts of the automobile body or other substrates, such as box sections. Auxiliary electrodes can be used if desired to enable the coating composition to reach the furthest parts reached by the best commercial cathodic electro-coating composition.

Cured coatings produced according to the invention are generally much tougher and more resistant to scab corrosion than coatings based on cationic electropaints with no added powder. The coatings of the invention are also more resistant to corrosion by salt spray, as shown by tests in which a coating on a steel panel is scratched to the metal and subjected to a salt spray test; growth of filiform corrosion from the scratch is reduced.

The coatings of the invention are also useful for electro-coating articles other than automobile bodies and body components. Central-heating radiators, for example, have complex flutes and grooves which can be electro-coated by a composition of good throwing power. The electro-coating is not usually overcoated in the instance. The coating composition of the invention can be used to electro-coat radiators to produce a white coating with good covering power and colour stability.

The process of the invention can also be used to provide a tough cured film in a single coating step, for example for agricultural and industrial machinery. The coating has good abrasion resistance,

corrosion resistance and opacity and the coating composition has sufficient throwing power to coat all surfaces of most types of agricultural machinery. Acrylic copolymer cationic binder resins having amine and hydroxyl groups, used with an aliphatic blocked isocyanate curing agent and a thermo-setting polyurethane resin powder, are particularly preferred for uses such as on agricultural machinery where exterior durability is important.

The invention is illustrated by the following Examples:—

EXAMPLE 1

(a) A thermo-setting resin powder of the following composition:—

| | Parts by Weight |
|---|---|
| Rutile titanium dioxide | 35.40 |
| Dow DER 663 U epoxy resin | 54.64 |
| Dow DER 673 MF epoxy resin | 7.12 |
| dicyandiamide | 1.42 |
| accelerated dicyandiamide | 1.42 |

was made by pre-mixing the ingredients, extruding and fine grinding to give a powder having a mean particle size of 40 microns. Both the epoxy resins are bisphenol A epichlorhydrin condensates. DER 663 U has an epoxy equivalent weight of about 785.

(b) A cationic, amino-substituted epoxy resin binder was prepared by reacting the following ingredients:

| | Parts by Weight |
|---|---|
| Epikote 1001 epoxy resin | 48.21 |
| Diethanolamine | 10.37 |
| Isopropanol solvent | 29.70 |

at 75—80°C for $2\frac{1}{2}$ hours. 11.72 parts by weight Crelan U1 curing agent were then added and allowed to dissolve in the resin solution. Epikote 1001 is a bisphenol A epichlorhydrin condensate having a molecular weight of about 500. Crelan U1 is an aliphatic blocked diisocyanate commercially available from Bayer.

(c) The following dispersion was then made:—

| | Parts by Weight |
|---|---|
| epoxy-amino resin solution (prepared in (b) above) | 406 |
| acetic acid solution (25% w/w) | 61 |
| demineralised water | 729 |
| thermo-setting resin powder (prepared in (a) above) | 227 |
| rutile titanium dioxide | 67 |

the above ingredients were dispersed by milling in a ceramic ball mill for 16—20 hours. The product was diluted with demineralised water to give a dispersion having a solids content of 12 *per cent* by weight. The dispersion had the following properties:—

| | |
|---|---|
| pH | 6.0 |
| Conductivity | 1500 μmhos |
| Weight ratio of total pigment to total resins (cationic binder plus powder) | 1:2.9 |
| Weight ratio of thermo-setting resin powder to cationic binder resin | 0.8:1.0 |

The dispersion was then transferred to an electro-deposition bath. A zinc phosphated steel panel to be painted was immersed in the bath as the cathode. An anode of stainless steel was also immersed. Electro-deposition was carried out at 25°C at an applied voltage of 250 V for 2½ minutes. The coated panel was then rinsed with water and baked at 180°C for 15 minutes. The resulting coating was smooth and of good appearance.

The properties of the coating are summarised in Table 1.

EXAMPLE 2

(a) A thermo-setting resin powder coating having the same composition as that used in Example 1 was made.

(b) A cationic, amino-substituted epoxy resin binder was prepared from the following ingredients:—

| | Parts by Weight |
|---|---|
| Epikote 1001 epoxy resin | 44.09 |
| Isopropanol | 29.56 |
| Diethanolamine | 6.09 |
| Diethylenetriamine | 3.98 |
| Crelan U1 blocked diisocyanate | 16.28 |

The epoxy resin was dissolved in the isopropanol at 75—80°C. The diethanolamine was then added and allowed to react for one hour at 75—80°C. The diethylenetriamine was added and the mixture allowed to react at 80°C for three hours. Finally the Crelan U1 was added and allowed to dissolve in the resin solution.

(c) The following dispersion was then made:—

| | Parts by Weight |
|---|---|
| epoxy-amino resin solution (prepared in (b) above) | 143 |
| acetic acid (25% w/w) | 37 |
| demineralised water | 260 |
| thermo-setting resin powder (prepared in (a) above) | 60 |
| rutile titanium dioxide | 25 |

The above ingredients were dispersed by milling in a ceramic ball mill for 16—24 hours. This was then diluted to 12% by weight solids content with demineralised water.

The dispersion had the following properties:—

| | |
|---|---|
| pH | 5.8 |
| Conductivity | 1600 μmhos |
| Weight ratio of total pigment to total resins (cationic binder plus powder) | 1:3 |
| Weight ratio of thermo-setting resin powder to cationic binder resin | 0.6:1.0 |

Electro-deposition was then carried out as described in Example 1.

The properties of the coatings are summarised in Table 1.

TABLE 1

| | Example 1 | Example 2 |
|---|---|---|
| Film thickness | 35—40 microns | 45—50 microns |
| Appearance | Good | Slight orange peel |
| Humidity resistance — 168 hours | No blistering | No blistering |
| Water soak resistance — 500 hours at 100°F (38°C) | No loss of adhesion | No loss of adhesion |
| Salt spray resistance — 500 hours ASTMS B117 | Maximum creep 1 mm no blistering | Maximum creep 1 mm no blistering |
| Throwing power (30 cm represents maximum throw) | 20 cm | 22 cm |
| Resistance to stone chipping | Good | Good |

The "creep" in the salt spray resistance test is the maximum growth of corrosion away from a scribe in the coating.

The throwing power is the distance coated up the inside surfaces of two cathode substrate panels spaced 6 mm apart and shielded from the anode.

CLAIMS

1. An aqueous composition suitable for cathodic electro-deposition comprising a cationic binder resin, a curing agent for heat curing the cationic binder resin after electro-deposition and a fusible solid thermo-setting resin powder dispersed in the coating composition, the weight of thermo-setting resin powder being 10 to 100 *per cent* based on the weight of the cationic binder resin and the curing agent therefor.

2. A coating composition according to claim 1 in which the cationic binder resin is an epoxy resin containing amine groups.

3. A coating composition according to claim 2 in which the cationic binder resin is an epoxy resin containing amine and hydroxyl groups and is the reaction product of a condensed glycidyl ether of a bisphenol and a hydroxyalkyl amine.

4. A coating composition according to claim 2 in which the cationic binder resin is the reaction product of an epoxy resin and a polyamine having both secondary and primary amine groups.

5. A coating composition according to claim 2 in which the cationic binder resin is the reaction product of an epoxy resin with a hydroxyalkyl amine and a polyamine having both secondary and primary amine groups.

6. A coating composition according to any of claims 1 to 5 in which the curing agent for the cationic binder resin contains blocked isocyanate groups.

7. A coating composition according to claim 6 in which the curing agent for the cationic binder resin is an aliphatic polyisocyanate whose isocyanate groups are blocked by reaction with a lactam.

8. A coating composition according to any of claims 2 to 7 in which the thermo-setting resin powder is an epoxy resin.

9. A coating composition according to claim 8 in which the thermo-setting epoxy resin powder incorporates dicyandiamide or a substituted dicyandiamide as curing agent for the epoxy resin powder.

10. A coating composition according to claim 1 in which the cationic binder resin is an acrylic copolymer containing amine and hydroxyl groups and the thermo-setting resin powder is based on a polyurethane prepolymer.

11. A coating composition according to any of claims 1 to 10 in which the weight of thermo-setting resin powder is 50 to 100 *per cent* based on the weight of the cationic binder resin and the curing agent therefor.

12. A coating composition according to any of claims 1 to 11 in which the thermo-setting resin powder contains a light coloured pigment within the powder particles.

13. A coating composition according to claim 12 in which the thermo-setting resin powder particles contain 5 to 50 *per cent* by weight titanium dioxide.

14. An aqueous coating composition suitable for cathodic electro-deposition comprising a cationic

binder resin, a curing agent and a thermo-setting resin powder substantially as described in either of the foregoing Examples.

15. A process for coating an electrically conductive substrate comprising immersing the substrate as cathode in an electro-coating bath of an aqueous coating composition according to any of claims 1 to 14, applying a voltage of 100 to 500 volts between an anode in the bath and the substrate as cathode to deposit a coating of the cationic binder resin, the curing agent and the thermo-setting resin powder on the substrate, removing the coated substrate from the bath and heating it at a temperature in the range 150 to 250°C to cure the cationic binder resin and to fuse and cure the thermo-setting resin powder.

16. A coating process according to claim 15 in which the pH of the coating composition is in the range 5 to 6.5.

17. A coating process according to claim 15 or 16 in which the applied voltage is 250 to 400 volts and the substrate is immersed as cathode in the electro-coating bath for 20 to 180 seconds to deposit a coating of dry film thickness 30 to 60 microns.

18. A coating process according to claim 17 in which the substrate is an automobile body or body component and the coated substrate is subsequently coated with a colour top coat without an intermediate surfacer coat.

19. A coating process according to claim 15 carried out substantially as hereinbefore specifically described or exemplified.

20. A car body, car body component or radiator coated by a coating process according to any of claims 15 to 19 to provide a coating having a dry film thickness of 20 to 60 microns.

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